INFLUENCE ON THE STRUCTURAL OPTICAL AND ELECTRICAL PROPERTIES OF CUPROUS IODIDE COMPLEXES WITH TETRAMETHYLETHYLENEDIAMINE

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INFLUENCE ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF COPPER IODIDE THIN FILM COMPLEXES WITH TETRAMETHYLETHYLENEDIAMINE

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ABSTRAK

Kajian ini akan cuba mengatasi kecenderungan kuprus iodida (CuI) untuk bersatu, cepat merosot, dan mudah tertanggal melalui teknik koordinasi kimia antara CuI dengan ligan organik alifatik yang dikenali sebagai N,N,N',N'-tetramethylethylenediamine (TMEDA). Pepejal kristal daripada kompleks CuI dengan TMEDA telah berjaya disintesis daripada larutan tepu dan homogen CuI dalam pelarut asetonitril. Pepejal yang disintesis berwarna coklat tetapi berubah dengan cepat menjadi pepejal biru gelap apabila terdedah kepada udara, menandakan sifat sensitif udara sebatian tersebut. Analisis FTIR mengesahkan kehadiran kumpulan berfungsi CH_2 dan CH_3, manakala analisis EDX mengesahkan stoikiometri $Cu_2I_2Tmeda_2$ kompleks terbabit. Puncak diffractogram sinar-X mengesahkan sifat pelbagai-kristal pepejal yang bertambah baik melalui pemanasan sederhana pada suhu 80 °C selama 15 minit. Kristalogri sampel merosot pada suhu 150 °C menunjukkan perubahan fasa telah berlaku melalui pengoksidaan CuI ke CuO. Kehadiran puncak diffractogram berorientasi (111) dan (200) menunjukkan pengekalan struktur CuI dalam sebatian. Pemerhatian FESEM menunjukkan sampel FTO bersalut seragam serta mengandungi butiran berbentuk monoklinik bertepatan dengan laporan sebelumnya, manakala saiz zarah agglomerasi ialah 3.03 μm. Pemerhatian TEM mendedahkan nanopartikel TMEDA berbentuk spherikal dan aglomerasi melindungi nanopartikel CuI yang lebih kecil. Spektroskopi optic menunjukkan penyerapan UV yang baik, ketelusan yang tinggi ke atas julat penglihatan, dan tenaga jurang band terus ~2.4 eV dengan suhu penyepuhlindapan pada 90 °C. Menggandakan kepekatan larutan menurunkan tenaga jurang band sebanyak 0.24 eV. Spektroskopi impedansi menunjukkan model penggabungan resapan dengan ciri Warburg berfrekuensi rendah, rintangan pengangkutan lubang 190 Ω, rintangan rekombinasi 5.73 kΩ, dan jangka hayat elektron selama 3.16 μs yang bertambah baik sebanyak dua julat magnitud apabila kepekatan diganda. Hasil kajian menunjukkan bahan berpotensi sebagai medium pengangkutan bagi cas positif.

ABSTRACT

This study will attempt to overcome the strong tendency of cuprous iodide (CuI) to coalesce, rapidly deteriorates, and detaches from interfacial contacts by chelating the CuI with an aliphatic organic ligand known as *N,N,N',N'*-tetramethylethylenediamine (TMEDA). Crystalline solids of CuI complexes with TMEDA is successfully synthesized from the saturated and homogenous solution of CuI in acetonitrile. The brown solids quickly turned to dark-blue once exposed to air indicating the air-sensitive nature of the compound. The FTIR confirms the presence of CH_2, and CH_3 functional group, while EDX analysis confirms the $Cu_2I_2Tmeda_2$ stoichiometry of the complex compound. X-ray diffractogram peaks confirm the multi-crystalline nature of the solid which improved after 15 minutes of moderate heating at 80°C. Sample loses its crystallinity at 150 °C suggesting a phase transition due to oxidation of CuI to CuO. The sharp peaks at (111) and (200) orientations remained after the complexation demonstrating that some of the CuI structure is retained. The FESEM observation shows the presence of monoclinic shaped grains as reported in the literatures, with an average agglomerated grain size of 3.03 μm as well as more uniform FTO coverage than the bare CuI sample. TEMs observation reveals the spherically shaped and agglomerated TMEDA nanoparticles shielding the much smaller CuI nanoparticles. Optical spectroscopy indicates good UV absorbance, high transparency over the visible range, and direct band gap energy of ~2.4 eV at an annealing temperature of 90 °C. Doubling the solution concentration lowers the band gap energy by ~ 0.24 eV. Impedance spectroscopy suggest a diffusion-recombination model with low frequency Warburg feature, hole transport resistance of 190 Ω, recombination resistance of 5.73 kΩ, and electron lifetime of 3.16 μs which improves by two orders of magnitude when the concentration doubles at 0.5 V forward bias. The findings suggest this material is potentially useful as hole transport medium.

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LIST OF SYMBOLS

A	Absorbance
$C\mu$	Chemical Capacitance
E_g	Band Gap Energy
f	Frequency
L	Litre
M, mM, μM	Molar, millimolar, micromolar
mol	Mole
n	Carrier Density
R	Reflectance
R_{ct}	Charge Transfer Resistance
R_{rec}	Recombination Resistance
R_{HTM}	Resistance in the Hole Transport Material
R_S	Series Resistance
T	Transmittance
V_{bi}	Biasing Potential
Z	Impedance
Z'	Real part of the Impedance
Z''	Imaginary part of the Impedance
α	Absorption Coefficient
ε	Dielectric Constant
μ	Mobility

LIST OF ABBREVIATIONS

ABP	Amino-bromo-pyrimidine
ACN	Acetonitrile (solvent)
ADC	Analogue to Digital Converter
AFM	Atomic force microscopy
APM	Aminopyrimidines
BZ	Benzoyl
BZPY	Benzoylpyridine
C	Carbon
Ca	Calcium
CE	Auxiliary or Counter Electrode
CH_3	Methyl
CPE	Constant Phase Element
Cu^+	Copper(I)
Cu^{2+}	Copper(II)
Cu	Copper
Cu^+	Copper Cation
CuI	Copper(I) Iodide / Cuprous Iodide
DABCO	Diazabicyclooctane
DAC	Digital to Analogue Converter
DC	Direct Current
De	Diethyl
DMG	Diffraction Grating Monochromator
DMSO	Dimethyl sulfoxide (basic solvent)
DSSC	Dye-Sensitized Solar Cell
EDL	Electrical Double Layer
EDS	Energy Dispersive X-Ray Spectroscopy
EDX	Energy Dispersive X-Ray
EIS	Electrochemical Impedance Spectroscopy
EN	Ethylenediamine
Et	Ethyl
ETA	2-aminoethanol

ETL	Electron Transport Layer
EtOH	Ethanol
FCC	Face Centered Cubic
FESEM	Field Emission Scanning Electron Microscopy
FRA	Frequency Response Analyzer
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine Doped Tin Oxide
H	Hydrogen
HI	Hydroiodide Acid
HTL	Holes Transport Layer
HTM	Holes Transport Medium
I	Iodine
I^-	Iodide
I_3^-	Triiodide
IMID	Imidazole
ITO	Indium Doped Tin Oxide
KI	Potassium Iodide
M	Molar
Me	Methyl
ME	2-methoxyethanol
MeCN	Acetonitrile
ML	Molecular Liquid
MOF	Metal Organic Framework
MW	Molecular Weight
N	Nitrogen
NIR	Near Infra-red
NS	Nano Structured
O	Oxygen
OLE	Organic Liquid Electrolyte
PHEN	Phenanthroline
PL	Photoluminescence
PMT	Photon Multiplier/Detector
PY	Pyridine

PYZ	Pyrazine
QUINZ	Quinazoline
RE	Reference Electrode
RI	Refractive Index
RT	Room Temperature
S	Sense Electrode
SC	Spin Orbit
SCN^-	Thiocyanate anion
Si	Silicon
SMN	Supramolecular Network
SSDSSC	Solid-State Dye-Sensitized Solar Cell
TADF	Thermally Activated Delayed Fluorescence
TCO	Transparent Conducting Oxide
TEM	Transmission Electron Microscopy
TL	Transmission Line
TMEDA	N,N,N',N'-tetramethylethylenediamine
UV	Ultra-violet
UV-Vis-NIR	Ultra-violet Visual and Near-infra-red Spectroscopy
Vis	Visual
WBS	Wide Band Gap Semiconductor
WE	Working or Indicator Electrode
XRD	X-ray diffractometry

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